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(56) Documents Cited
GB 2234754 A GB 2232986 A GB 2231333 A
GB 2220208 A GB 2213813 A GB 2203157 A
GB 2188643 A EP 0393813 A1 EP 0339760 A1
EP 0249010 A2

(58) Field of Search
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(54) Fire-retardent material

(57) Fire-retardant material in shaped form which retains its structural integrity after degradation of its organic content in a fire is made by curing a shaped mass of curable elastomer (eg an ethylene/vinyl acetate copolymer) in which are dispersed (i) a mixture of glass-formers ("frits") melting progressively over a range of several hundred degrees C and containing components which devitrify in the upper part of the range, (ii) aluminium hydroxide and (iii) a magnesium compound (eg $Mg(OH)_2$ endothermically decomposable to magnesium oxide.

The mixture of frits preferably forms less than 15% by weight of the material.

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Fire-retardant material

This invention relates to fire-retardant material, and more particularly to such material in shaped form, for example in the form of sheet.

It is well known to make shaped material of a polymer or polymers rendered fire-retardant by the incorporation of halogenated compounds and phosphorus compounds. In a fire, however, toxic smoke and corrosive gas are evolved from such fire-retardant material.

A product recently introduced onto the market makes it possible to avoid this in large measure. The product, which is sold by Brunner Mond & Co under the registered trade mark CEEPREE, is a mixture of glass-formers ("frits") which are so varied in chemical composition that the mixture melts progressively over a range of several hundred degrees Celsius. Typically (see the Brunner Mond publication No 5.92/2M/UK/1) the lowest melting components of the vitreous mixture (frits mixture) begin to melt at around 350°C. At much higher temperatures - in the upper part of the range, eg 800 - 900°C - certain components of the mixture

devitrify: that is, they pass from the glassy state to a crystalline state. When incorporated into material moulded from polymers such as thermoset resins (eg polyesters and epoxies) and thermoplastic resins (eg polypropylene and polyamides), the frits mixture brings about a significantly improved resistance to fire, but without causing evolution of toxic vapours. In a fire, the organic content of the moulded material becomes degraded, ie it chars and eventually burns out; but in spite of this the structural integrity of the material is retained even at 1000°C and higher, presumably because of the bonding effect of the glass or the devitrified matter formed from it. This is of importance in reducing the extent to which flame and hot gases can pass through the structure at high temperature, and is thus important in reducing the propagation of fire.

We have experimented with the inclusion of frits mixtures in polymeric material which is elastomer-based, and have found that the fire-retardant properties then conferred on such material can be improved to an unexpected extent by the additional inclusion of aluminium hydroxide (sometimes known as "alumina trihydrate") and certain magnesium compounds, while keeping the weight proportion of the frits mixture (a relatively high-cost material) below 15% of the product.

According to the invention, there is provided fire-retardant material in shaped form which retains its structural integrity after degradation of its organic content in a fire, made by curing a shaped mass of curable elastomer in which are dispersed

(i) a mixture of frits melting progressively over a range of several hundred degrees C and containing components which devitrify in the upper part of the range, (ii) aluminium hydroxide and (iii) a magnesium compound endothermically decomposable to magnesium oxide; the mixture of frits forming less than 15% by weight of the material.

The magnesium compound just referred to is preferably magnesium hydroxide, but there may alternatively be used a magnesium carbonate (eg magnesite, $MgCO_3$), dolomite ($MgCO_3 . CaCO_3$), the hydrated basic magnesium carbonate of commerce containing the equivalent of 40% MgO, or the material sold under the trade mark ULTRACARB, being a mixture of $Mg_3 Ca (CO_3)_4$ and $Mg_4 (CO_3)_3 (OH)_2 .3H_2O$. (Magnesium compounds such as the nitrate, which generate toxic fumes on ignition, should not be used.)

Very useful fire-retardant properties are obtainable by keeping the weight proportion of the frits mixture below 10% of the product.

The elastomer employed may for example be styrene butadiene rubber, polyisobutylene, polynorbornene, natural rubber, ethylene copolymers such as ethylene/vinyl acetate copolymers of the kind with elastomeric properties, or mixtures of these materials.

Preferred proportions of the frits mixture : (aluminium hydroxide + magnesium compound) are in the range 1:15 - 1:3 by weight.

The fire retardant material may contain fillers of the kind conventionally employed in this field, for example calcium silicate, silica or china clay.

According to another feature of the invention, a process for the manufacture of a shaped fire-retardant material comprises mechanically working (as for example in a Banbury mixer) the frits and aluminium hydroxide and magnesium compound with the curable elastomer, and heating in shaped form the mixture thus obtained, to cure the elastomer.

The products of the invention are useful in a wide variety of situations where it is desirable to provide specially against spread of fire; for example, as cable covering, as floor covering in transport vehicles, as a vertical fire barrier (whether alone or as part of a low-weight composite), and as glazing beads for fire doors. It is noteworthy that in such applications there is no need to provide fibre reinforcement (such as glass fibre which is employed in many comparable products which are at present in use.

The invention is further illustrated by the following Example, which relates to the production of sheet suitable for use as flooring material in the vehicles of mass transit systems, for example Underground trains.

Example

A mixture of the following materials was prepared:

	Parts by weight
Ethylene/vinyl acetate copolymer (melt flow index 45-70 dg/min; wt % vinyl acetate content, 40)	100
Mixture of frits sold under the trade mark CEEPREE (Brunner Mond & Co), grade C200, melting point range 350-900°C	25
Aluminium hydroxide, median particle size, 1μm, specific surface area 11m²/g	170
Magnesium hydroxide, particle size < 1μm; specific surface area 20 m²/g	120
Fillers (china clay and silica flour BS240 mesh)	65
Pigment	10
Elastomer-curing agent	10
TOTAL:	500

The ethylene/vinyl acetate copolymer was shear-mixed in a Banbury mixer with other substances listed, and the mixture thus formed was discharged and formed conventionally into a band, which was then cut into squares and cooled. The cooled material was granulated, and the granular product was extruded in an Iddon extruder (die temperature, 90°C) to form flat sheet (still uncured) of thickness 2.5mm. This was passed through a cooling bath, then through a bath of anti-stick agent. Finally, curing was carried out by heating at 140°C. This may be done by press-curing, autoclaving or rotocuring.

The flexible sheet product had the following properties:

Thickness (mm)	2.3
Density (g/cm^3)	1.86
Ultimate tensile strength (MPa)	10-12
Elongation at break (%)	40-45
Hardness (BS 3260 : 1969)	Residual indentation
	< 0.15mm
Abrasive wear (MOAT 2)	Suitable for heavy wear

In a fire test conducted in accordance with BS 475, Pt 20: 1987, the flexible sheet product, despite the loss of its elastomer content by combustion - retained its integrity at 1200°C, indicating its usefulness as the outer (exposed) layer of a fire barrier in addition to its flooring applications. Such a fire barrier might, for example, take the form of a sandwich of foamed phenol formaldehyde resin between surface layers prepared as above.

CLAIMS

1. Fire-retardant material in shaped form which retains its structural integrity after degradation of its organic content in a fire, made by curing a shaped mass of curable elastomer in which are dispersed (i) a mixture of frits melting progressively over a range of several hundred degrees C and containing components which devitrify in the upper part of the range, (ii) aluminium hydroxide, and (iii) a magnesium compound endothermically decomposable to magnesium oxide; in which material the mixture of frits forms less than 15% by weight.

2. Fire-retardant material according to claim 1, in which the magnesium compound is magnesium hydroxide.

3. Fire-retardant material according to claim 1 or 2, in which the mixture of frits forms less than 10% by weight.

4. Fire-retardant material according to any of claims 1 to 3, in which the curable elastomer is an ethylene/vinyl acetate copolymer.

5. Fire-retardant material according to any of claims 1 to 4, in the form of sheet.

6. A process for the manufacture of the fire-retardant material of any preceding claim, which comprises mechanically working the frits and aluminium hydroxide and magnesium compound with the curable elastomer, and heating in shaped form the mixture thus obtained, to cure the elastomer.

7. Fire-retardant material, and a process for its manufacture, substantially as described herein with reference to the Example.

Patents Act 1977
Examiner's report to the Comptroller under Section 17 (The Search Report)

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Relevant Technical fields

(i) UK Cl (Edition L) C3K (KEB, KEF, KEZ, KMA)
C3V (VDC, VDD, VDM, VDX)

(ii) Int Cl (Edition 5) C08K; C09K

Search Examiner
A J RUDGE

Databases (see over)
(i) UK Patent Office

(ii) ONLINE DATABASES: WPI, CLAIMS

Date of Search
18 AUGUST 1993

Documents considered relevant following a search in respect of claims

Category (see over)	Identity of document and relevant passages		Relevant to claim(s)
X;Y	GB 2234754 A	(CROMPTON) See whole document	1,3,5,6
A	GB 2232986 A	(CROMPTON) See Claims and pages 1-3	All
Y	GB 2231333 A	(BOWTHORPE-HELLERMAN) See Claims 1, and 6-10	4
X;Y	GB 2220208 A	(CROMPTON) See whole document	1,3,6; 1-8
X;Y	GB 2213813 A	(CROMPTON) eg Claims 6,10,16 and page 2, line 23, et seq	1,3,5-7; 1-8
X;Y	GB 2203157 A	(CROMPTON) eg Claims 1,5 and page 3, line 2 et seq	1,3,5-7; 1-8
X;Y	GB 2188643 A	(CROMPTON) eg Claims 3,5,6,8	1;5
Y	EP 0393813 A1	(FURUKAWA) eg Claims 1,3,13	1,5
X	EP 0339760 A1	(M&T) See whole document	1-8
Y	EP 0249010 A2	(CHEMISCHE FABRIK) eg Claims and examples	5

Category	Identity of document and relevant passages -10-	Relevant to claim(s)

Categories of documents

X: Document indicating lack of novelty or of inventive step.

Y: Document indicating lack of inventive step if combined with one or more other documents of the same category.

A: Document indicating technological background and/or state of the art.

P: Document published on or after the declared priority date but before the filing date of the present application.

E: Patent document published on or after, but with priority date earlier than, the filing date of the present application.

&: Member of the same patent family, corresponding document.

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